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FINAL TECHNICAL REPORT

to

Air Force Office of Scientific Research

Anionic Conducting Oxide Ceramics

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Program Manager: Dr. Alexander Pechenik

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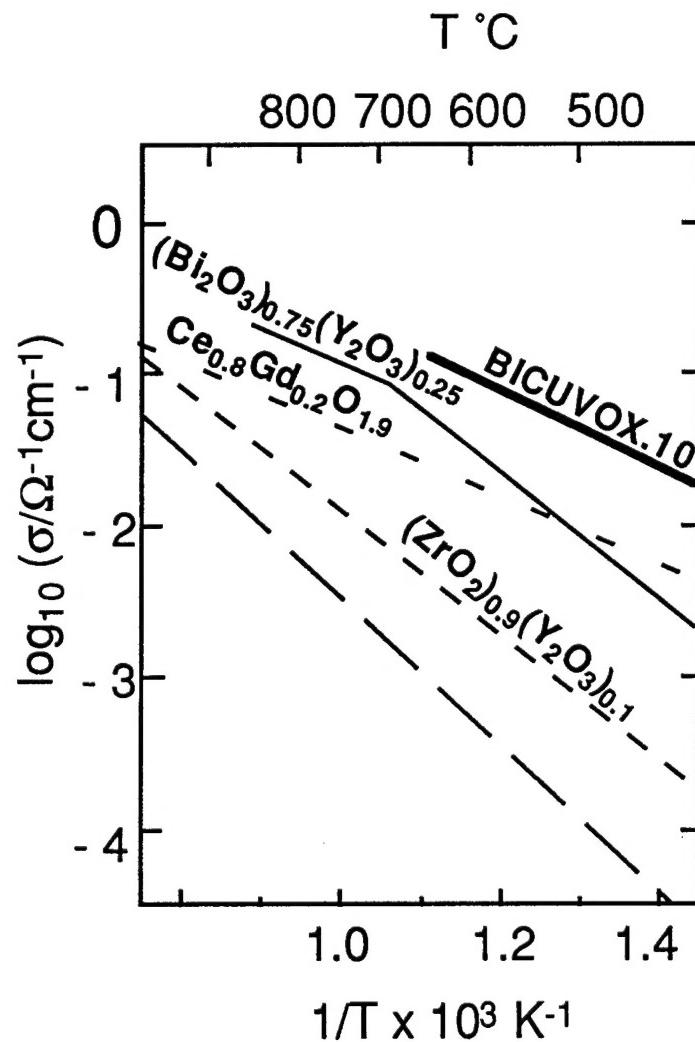
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Abstract

This program has emphasized the interrelationships among synthesis, microstructure and properties for oxygen ion conducting ceramics based on copper-substituted bismuth vanadate ($\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.1}\text{O}_{5.35}$), known as BICUVOX. We showed that these materials readily formed dense ceramics with equiaxed microstructures and confirmed that they exhibited high ionic conductivity. Prolonged heat treatments at elevated temperatures did not cause significant changes in conductivity, an important consideration for electrochemical device operation. We also developed solution processing approaches for preparing thin films of the bismuth vanadate materials.

1. Introduction

There has long been an interest in finding oxygen ion conducting solids that exhibit high



conductivities at low temperatures for use in a variety of electrochemical devices including fuel cells, oxygen sensors and oxygen pumps. For the most part, such applications were based on stabilized zirconia and other oxides that crystallize in the fluorite structure (e.g., CeO_2).¹ In the 1970's and 1980's a number of Bi_2O_3 based systems were shown to exhibit significantly higher conductivities than zirconia over the temperature range 500 to 700°C.^{2,3} The application of the Bi_2O_3 electrolytes was somewhat limited, however, because of fairly rapid reduction of these materials under low oxygen partial pressure. More recently, a new group of low

Figure 1. Arrhenius plot showing the high conductivity of copper-doped bismuth vanadate compared to fluorite oxygen ion conductors.

temperature O²⁻ conducting materials based on bismuth vanadate (Bi₄V₂O₁₁) has emerged. Interestingly, these materials have a layer structure and a tetragonal unit cell in contrast to the cubic structure of the fluorite systems and yet achieve conductivities in excess of 10⁻² S/cm at 400°C.^{4,5,6} This is some least 50 to 100 times larger than any other oxygen ion conductor in this temperature range. The Arrhenius plots for several different oxygen ion conductors are compared to stabilized zirconia in Figure 1.

In this research program we have emphasized the interrelationships among synthesis, microstructure and properties of the bismuth vanadate system.^{7,8} In previous annual progress reports we showed that these materials readily formed dense ceramics with equiaxed microstructures and confirmed that they exhibited high ionic conductivity. We also described solution processing approaches for preparing powders and thin films of the conductive bismuth vanadate materials.⁸ In this final report, we focus on the synthesis and characterization of thin films, including the first measurements of their transport properties.

2. Synthesis of BICUVOX Thin Films

Our most recent research efforts have been directed at developing solution processing routes for synthesizing thin films of BICUVOX. One of the most common means of lowering the resistive losses in electrochemical devices is to utilize a thin film configuration. Solution routes to preparing thin films are relatively new, but represent a viable alternative to more costly vapor-phase methods.⁹ The following sections briefly review our results on the processing, microstructure and properties of BICUVOX thin films.

Thin films were prepared using metal ethylhexanoates and isopropoxide organic precursors. This approach is similar to one used to synthesize both Bi-Sr-Ca-Cu-O and Y-Ba-Cu-O superconductors.¹⁰ The principal advantage of this route is that it produces a homogeneous solution which may then be used in the preparation of BICUVOX thin films. To form the precursor solution, appropriate amounts of bismuth 2-ethylhexanoate (Bi[C₄H₉CH(C₂H₅)COO]₃), copper 2-ethylhexanoate ([CH₃(CH₂)₃CH(C₂H₅)CO₂]₂Cu) and vanadium triisopropoxide (C₃H₁₂O₄V) were added to chloroform and stirred at room temperature to form a clear dark green solution. Thin films were formed by spin coating the solution onto various substrate materials and then pyrolyzing to decompose the organics and produce the BICUVOX phase. Sintering of the films was carried out at 800°C for 10 minutes. A flow chart for the preparation of BICUVOX films is shown in Fig. 2.

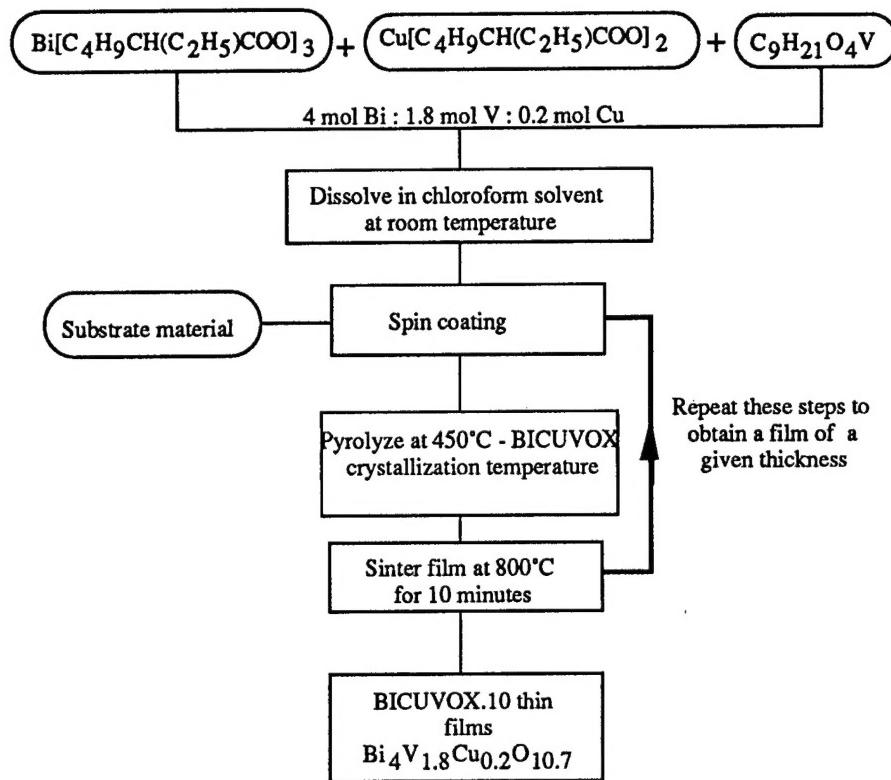


Figure 2. Flow chart showing the steps used in the processing of BICUVOX thin films from metal organic precursors.

Thermogravimetric analysis (TGA) of the precursor solution indicates a significant weight loss from 125°C to 265°C, which corresponds to the combined removal of any remaining water or chloroform.⁸ Above 265°C a very small amount of weight is lost and might signify decomposition of the organic components in the precursor resin. The DTA curve for the precursor indicates a relatively broad exothermic peak from 300-400°C with no additional peaks up to 800°C. This implies that the organic decomposition and phase formation processes were effectively complete at temperatures as low as 400°C.

We have used atomic force microscopy (AFM) to provide details concerning microstructure development of the thin films. In our experiments, a single layer thin film (thickness ≈ 2000 Å) was heated to 550°C and, after cooling, examined using the AFM. Following the AFM scan, the same sample was reheated to 650°C, similarly examined and so on. Figure 3 shows AFM micrographs indicating grain growth in the BICUVOX thin film over the temperature range 550°C to 800°C. As expected, higher sintering temperatures yield larger grain sizes. However, it is interesting to note that the grain size of the films is significantly greater than the thickness of the film. This suggests that the grain growth is 2-dimensional in nature. At some point the grains become larger than the thickness of the film and must grow in a 2-dimensional fashion in order to produce the observed microstructure.

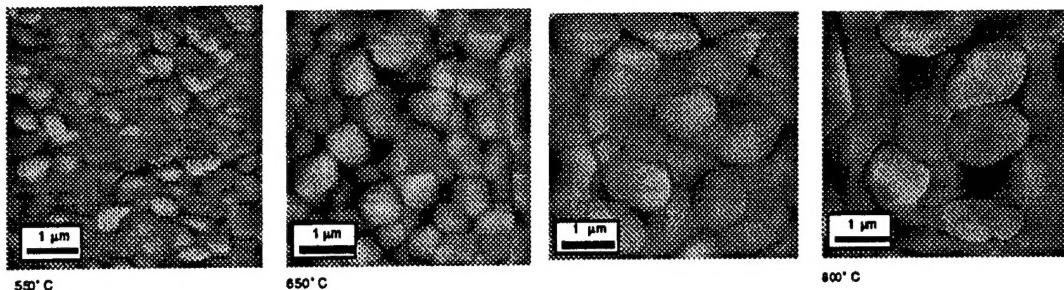


Figure 3. Topographic AFM images indicating grain growth characteristics of a single BICUVOX film at 550°C, 650°C, 750°C, and 800°C, respectively.

Another interesting consideration in the present study is the influence of different substrate materials on film microstructure. BICUVOX thin films were produced using the metal-organic precursor solution and spin coating onto a variety of substrate materials including polycrystalline alumina, polycrystalline and single crystal MgO (100), polycrystalline yttria-stabilized zirconia (YSZ) and single crystal SrTiO₃ (100). Depending on the type of substrate and the processing procedures, crystalline films with different morphologies were obtained. For these investigations, films were spun at room temperature and then heated at 10°C/min to 800°C and sintered for 10 minutes before cooling down to room temperature. The results indicate that thermal expansion differences and reactivity between the film and substrate have a profound influence on film microstructure. Cracks were observed in the films deposited on Al₂O₃ and YSZ substrates. Not surprisingly, the cracks were much more pronounced for Al₂O₃ which has a thermal expansion coefficient approximately half that of BICUVOX. Significant cracking was not observed for films on MgO since the thermal mismatch between substrate and film is relatively small and induced strains can be more easily accommodated within the film. SrTiO₃ ($a = 3.90 \text{ \AA}$) represents an excellent lattice match to BICUVOX, however, there is evidence of reaction between the film and the substrate. The results with SrTiO₃ substrates underscore the importance of selecting substrate materials which avoid reaction with the BICUVOX phase.

The good mechanical integrity of the films prepared on MgO substrates suggests the possibility of growing single crystal films of BICUVOX on MgO single crystals. Although the lattice mismatch between cubic MgO ($a = 4.216 \text{ \AA}$) and tetragonal BICUVOX ($a = 3.907 \text{ \AA}$) is in excess of 7%, epitaxial mechanisms have been studied for systems exhibiting such large mismatches.⁹ Initial experiments for BICUVOX films grown on single crystal MgO substrates indicate a high degree of crystal orientation. Fig. 4 shows significant enhancement of peak intensities for the (002) and (006) reflections for a thin film on single crystal MgO as compared to a BICUVOX powder.

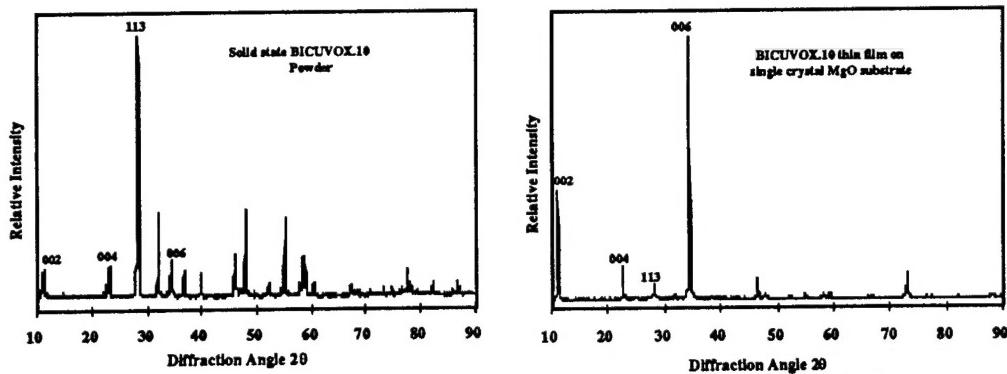


Figure 4. XRD comparing a thin film spin-coated onto a single crystal MgO substrate and a polycrystalline powder sample.

Impedance measurements were made on thin film samples in the plane of the film. In view of the preferred orientation developed in these films, these measurements were made along the high conductivity pathway (i.e., along the *ab*-plane). Measurements were made from 200°C to 600°C in both heating and cooling modes at 50°C intervals. The impedance data from a measurement at 350°C is shown in Fig. 5 in the form of a Nyquist plot. The well resolved semi-circle is convenient for interpretation; the intersection of the curve with the real axis defines the resistive component of the total impedance. This resistive component, which includes both intragrain and grain boundary contributions, was used to derive the conductivity values as a function of temperature for the BICUVO_x thin film samples.

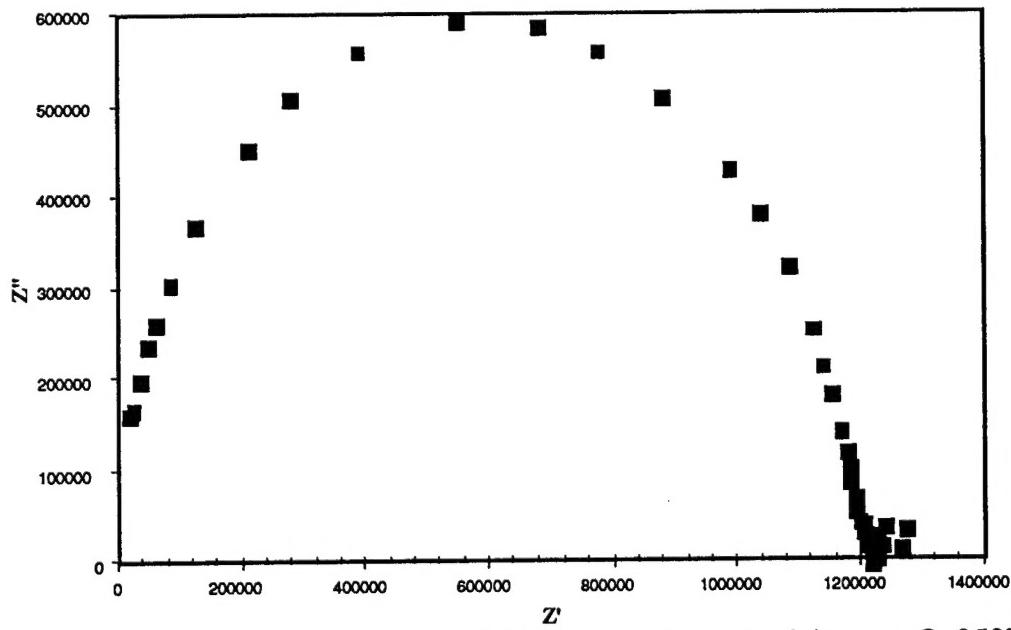


Figure 5. Nyquist plot from a "parallel-to-*ab* plane" conductivity test @ 350°C, cooling from 600°C.

As shown in Fig. 6, the temperature dependence of the conductivity can be represented by an Arrhenius equation:

$$\sigma = (\sigma_0/T) \exp(-E_a/kT) \quad (1)$$

where σ_0 = a pre-exponential constant, E_a = activation energy (eV), k = Boltzman constant and T is the temperature (K). The Arrhenius plot in Fig. 6 compares the conductivity for a dense BICUVOX ceramic with that of a thin film.

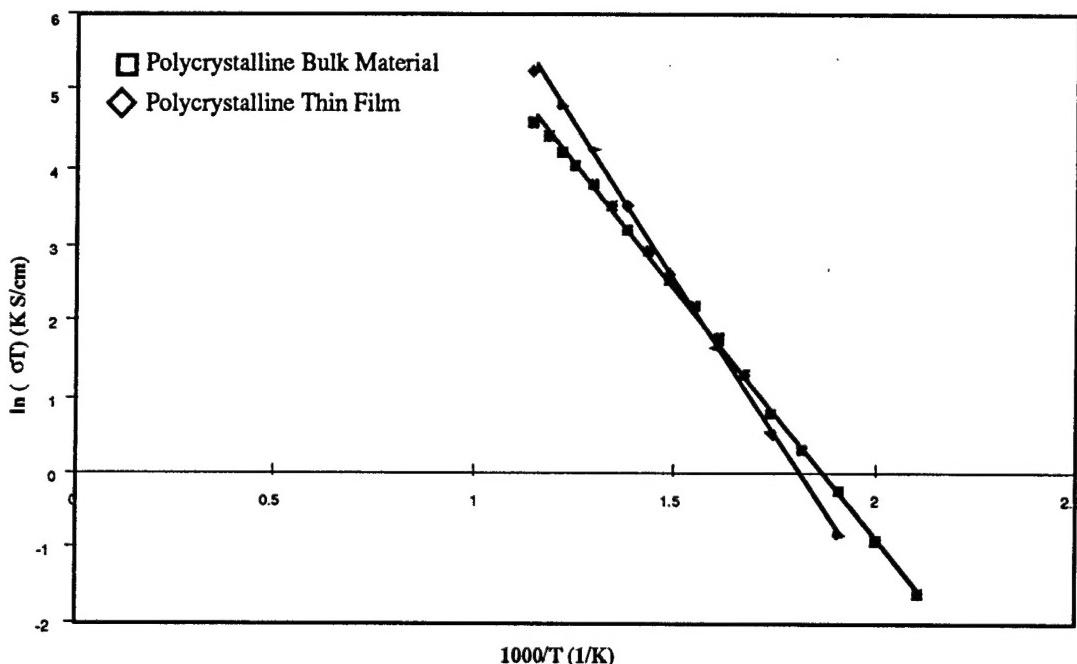


Figure 5: An Arrhenius plot comparing the conductivity and activation energy between a "parallel-to-*ab* plane" thin film sample and a bulk material sample.

There are two interesting features evident in this data. First, the thin film sample exhibits a higher activation energy than that of the ceramic and there is no change in activation energy. This suggests that the film is in the 'ordered' (γ') phase and that the $\gamma \rightarrow \gamma'$ phase transition has been suppressed. The second significant feature is that at temperatures above 400°C, the film exhibits a higher conductivity than that of the ceramic. This characteristic indicates that the preferred orientation in the film can lead to anisotropic conductivity in these materials. The latter result is significant because it suggests that with proper control of orientation, it will be possible to obtain thin films whose conductivities approach single crystal values.

REFERENCES

1. B.C.H. Steele in *High Conductivity Solid Electrolytes*, ed. by T. Takahashi, (World Scientific Press, Singapore, 1989) pp. 406-446.
2. M.J. Verkerk and A.J. Burggraaf, J. Electrochem. Soc. 128 (1981) 75
3. J.B. Goodenough, J.E. Ruiz-Diaz and Y.S. Zhen, Solid State Ionics 40/41 (1990) 21.
4. F. Abraham, M.F. Debremille-Gresse, G. Mairesse and G. Nowogrocki, Solid State Ionics 28-30 (1988) 529.
5. F. Abraham, J.C. Boivin, G. Mairesse and G. Nowogrocki, Solid State Ionics 40/41 (1990) 934.
6. R.N. Vannier, G. Mairesse, F. Abraham, G. Nowogrocki, E. Pernot, M. Anne, M. Bacmann, P. Strobel and J. Fouletier, Solid State Ionics 78, 183 (1995).
7. S.P. Simner, D. Suarez-Sandoval, J.D. Mackenzie and B. Dunn, J. Am. Ceram. Soc. 80, 2563 (1997)
8. S.P. Simner, P-W Wu and B. Dunn, J. Mater. Res. 13, 866 (1998)
9. F.F. Lange, Science, 1996, 273: 903-909.
10. S.J. Golden, T.E. Bloomer, F.F. Lange, A.M. Segadaes, K.J. Vaidya and A.K. Cheetham, Journal of American Ceramic Society, 1991, 74: 123-129.

Personnel Supported

Professors Bruce Dunn and J.D. Mackenzie are the Principal Investigator and Co-Principal Investigator, respectively, for this project. During the project period the following individuals were the principal contributors to the research: Dr. Steven Simner and Dr. Thomas Barrera (post-doctoral scholars), Mr. Peter Duong and Ms. Donaji Suarez-Sandoval (graduate students) and Mr. Joey Lin (undergraduate student).

Interactions with Armstrong Laboratory, Brooks AFB

There was substantial interaction and discussion of our work with the group headed by Capt. J. Fenner, Armstrong Laboratory, Brooks AFB. During the project period, this group began to establish a ceramic oxygen generator program and we transferred our methods and techniques to them in areas related to materials preparation and characterization. One especially significant feature is the use of the same software package in measurements of complex impedance. During the project period, there were several visits by Capt. Fenner and Lt. Edman to UCLA, and a few visits by Professor Dunn, Dr. Barrera and Dr. Simner to the Armstrong Laboratories. In addition, the UCLA group organized a three-day seminar for Brooks personnel (September 16-19, 1996) which reviewed the fundamentals of solid electrolytes and ceramic processing and discussed

technological aspects of oxygen generators. A one-day review with Brooks personnel was held at UCLA on November 14, 1997.

Publications and Presentations

- T.P. Barrera, B. Dunn, P.D. Fuqua, J. Leininger, J.D. Mackenzie, "Microstructure-Property Studies of BICUVOX Ceramics," Ceramic Transactions, Vol. 65, ed. by P.N. Kumta, G.S. Rohrer and U. Balachandran (American Ceramics Society, 1996) pp. 39-58
- S.P. Simner, D. Suarez-Sandoval, J.D. Mackenzie and B. Dunn, "Synthesis, Densification and Conductivity Characteristics of BICUVOX Oxygen Ion Conducting Ceramics", *J. American Ceramic Society* **80**, 2563 (1997)
- S.P. Simner, P-W. Wu and B. Dunn, "Solution Processing Approaches for Solid Electrolytes and Electrode Materials", *J. Mater. Research.* **13**, 866 (1998)
- T.A. Faltens, P.D. Fuqua, J. Leininger, J.D. Mackenzie and B. Dunn, "Microstructure-Property Studies of BICUVOX Ceramics, invited paper presented at American Ceramic Society, Cincinnati, Ohio, April, 1995.
- T.P. Barrera, J. Leininger, B. Dunn and J.D. Mackenzie, "Effects of Sintering Conditions on the Microstructure and Conductivity of BICUVOX Ceramics", American Ceramic Society, Seattle, WA. November, 1996.
- S.P. Simner, P-W. Wu and B. Dunn, "Solution Processing Approaches for Solid Electrolytes and Electrode Materials", invited paper presented at the 4th International Union of Materials Research Societies, Makuhari, Japan, September, 1997
- S. Simner and B. Dunn, "A Chemical Solution Route for Processing Thin Films of Oxygen Ion Conducting Bismuth Vanadate", presented at Ceramic Processing '97, Santa Barbara, CA. September, 1997
- S.P. Simner and B. Dunn, "Synthesis and Characterization of BICUVOX Oxygen Ion Conducting Ceramics, American Ceramic Society, San Francisco, November, 1997.

Honors/Awards

- J.D. Mackenzie received the Samuel R. Scholes Lecturer from Alfred University
- B. Dunn was appointed as an Associate Editor of the Journal of the American Ceramic Society
- B. Dunn received the 1995 Materials Science Award from the Department of Energy. The award recognizes research related to sol-gel deposition of thin films.
- B. Dunn was named a Fellow of the American Ceramics Society.